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(21) International Application Number: PCT/US00/08299 (22) International Filing Date: 30 March 2000 (30.03.00) (30) Priority Data: 60/127,465 31 March 1999 (31.03.99) US 60/161,659 21 October 1999 (21.10.99) US 09/499,690 8 February 2000 (08.02.00) US (63) Related by Continuation (CON) or Continuation-in-Part (CIP) to Earlier Applications US 60/161,659 (CON) Filed on 21 October 1999 (21.10.99) US 09/499,690 (CON) Filed on 8 February 2000 (08.02.00) US 60/127,465 (CON) Filed on 31 March 1999 (31.03.99) (71) Applicant (for all designated States except US): SYNTROLEUM CORPORATION [US/US]; Syntroleum Plaza, Suite 1100, 1350 South Boulder, Tulsa, OK 74119-3295 (US).		(72) Inventors; and (75) Inventors/Applicants (for US only): TOMLINSON, Harvard, L., Jr. [US/US]; 21 East 26th Street, Tulsa, OK 74114 (US). RUSSELL, J., Branch [US/US]; 9801 Knoxville Avenue, Tulsa, OK 74137 (US). (74) Agents: BELSER, Townsend, M., Jr.; Pollock, Vande Sande & Amernick, R.L.L.P., Suite 800, 1990 M Street, N.W., Washington, DC 20036-3425 (US) et al. (81) Designated States: AE, AL, AM, AT, AU, AZ, BA, BB, BG, BR, BY, CA, CH, CN, CR, CU, CZ, DE, DK, DM, EE, ES, FI, GB, GD, GE, GH, GM, HR, HU, ID, IL, IN, IS, JP, KE, KG, KP, KR, KZ, LC, LK, LR, LS, LT, LU, LV, MA, MD, MG, MK, MN, MW, MX, NO, NZ, PL, PT, RO, RU, SD, SE, SG, SI, SK, SL, TJ, TM, TR, TT, TZ, UA, UG, US, UZ, VN, YU, ZA, ZW, ARIPO patent (GH, GM, KE, LS, MW, SD, SL, SZ, TZ, UG, ZW), Eurasian patent (AM, AZ, BY, KG, KZ, MD, RU, TJ, TM), European patent (AT, BE, CH, CY, DE, DK, ES, FI, FR, GB, GR, IE, IT, LU, MC, NL, PT, SE), OAPI patent (BF, BJ, CF, CG, CI, CM, GA, GN, GW, ML, MR, NE, SN, TD, TG). Published <i>With international search report.</i> <i>Before the expiration of the time limit for amending the claims and to be republished in the event of the receipt of amendments.</i>	
(54) Title: FUEL-CELL FUELS, METHODS, AND SYSTEMS			
(57) Abstract A fuel cell fuel, a method of making a fuel cell fuel, a fuel cell system utilizing Fischer-Tropsch feed and a method of operating a fuel cell are disclosed. The fuel cell fuel is a light Fischer-Tropsch liquid having at least 77 wt.% normal and iso-paraffins, less than 20 wt.% olefins, less than 9 wt.% alcohols, less than 0.001 wt.% sulfur and less than 5 wt.% aromatics. The process of making the fuel cell fuel includes separating a heavy portion from a Fischer-Tropsch liquid, hydrocracking the heavy portion and separating a C ₅ -C ₁₈ portion from the hydrocrackate.			

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FUEL-CELL FUELS, METHODS, AND SYSTEMS

CROSS-REFERENCE TO RELATED APPLICATIONS

This application claims the benefit of the filing dates of, and fully incorporates by reference for all purposes, U.S. Patent Applications Serial Nos. 60/127,465, filed March 31, 1999 (provisional), 60/161,659, filed October 21, 1999 (provisional), and 09/499,690, filed February 8, 2000 (regular).

5 TECHNICAL FIELD OF THE INVENTION

The present invention relates to fuel cells, and more particularly, to fuel-cell fuels, to methods of making such fuels, and to fuel-cell powered systems, for example fuel cell systems powered by such fuels and light hydrocarbon conversion systems powered at least in part by fuel cells employing such fuels.

10 BACKGROUND OF THE INVENTION

Available technical literature indicates that fuels may be used in a fuel cell indirectly or directly, that is, with or without preliminary treatment in a fuel cell fuel processor, e.g., a reformer, to liberate hydrogen from the fuel. In the former case, which presently appears to be of principal interest to researchers, the processor and fuel cell cooperate, for example they may be fluidly inter-connected, to form a fuel cell system in which hydrogen liberated from fuel in the processor is fed to the fuel cell and there converted to electricity. In the latter case, the fuel cell system includes a fuel cell and possibly other components, but does not include a processor.

20 The present fuels of choice of the fuel cell industry are methanol, methane and propane, although interest has also been shown in gasoline derived from petroleum. Common forms of these fuels suffer from the hazards of, and/or the expenses of avoiding, one or more serious problems. Among these are fuel cell

catalyst-debilitating sulfur content, water solubility with ensuing environmental dangers, transportation and storage complications and unsuitability for distribution in existing distribution infrastructure. Continued interest in these fuels, despite their disadvantages, bears mute testimony to existence of an unfulfilled need for improved fuel cell fuels. The present invention is intended to address this need.

SUMMARY OF THE INVENTION

In a first aspect, the present invention includes a fuel cell fuel that may comprise or be composed substantially of synthetic products of Fischer-Tropsch processing, including paraffinic and optionally iso-paraffinic hydrocarbons, and containing less than 0.001 weight percent sulfur.

In one embodiment of the foregoing aspect, the fuel cell fuel contains less than 5 weight percent of aromatics.

In another embodiment of said aspect, the fuel cell fuel comprises tail gas of substantially C₅ or less.

In yet another embodiment of the above aspect, the fuel comprises liquids boiling in the range of C₅-C₂₀.

In still another embodiment of the first aspect, the fuel cell fuel comprises more hydrogen than C₄, preferably C₅ and more preferably C₆ hydrocarbon species, or more hydrogen than gasoline derived from petroleum.

In a second aspect, the present invention includes a fuel cell fuel which may comprise or be substantially composed of synthetic liquid, gaseous and/or vaporous products, preferably predominantly by weight liquid products, of Fischer-Tropsch processing, which have optionally been hydroisomerized and/or hydrocracked, including paraffinic and optionally iso-paraffinic hydrocarbons, having up to about 18, up to about 20 or up to about 22 carbon atoms.

In certain embodiments of either of the foregoing aspects, said fuel cell fuel may contain less than 5 weight percent or less than 1 weight percent of aromatics

5 In certain other embodiments of either of the foregoing aspects, said fuel cell fuel may contain small or substantial amounts of alcohols, if any, small or substantial amounts of unsaturates other than aromatics, if any, negligible amounts of S, and, preferably, only negligible amounts of N. In this context, negligible means insufficient in amount to require removal for successful use of the fuel containing same as a fuel cell fuel.

10 As is known to those skilled in the art, products of Fischer-Tropsch processing are products of methylene chain-propagating reactions of hydrogen and/or light hydrocarbons with CO in the presence of a methylene chain propagating catalyst(s), such as an iron, cobalt, rhenium or ruthenium catalyst of the types used in Fischer-Tropsch reactions, which are usually supported catalysts and may include promoters. Preferably, the reactions are conducted
15 under non-shifting conditions, which are described in the Fischer-Tropsch literature.

In the descriptions of the foregoing aspects and embodiments of the invention and in the descriptions of other aspects and embodiments of the invention which follow, indications that fuels or fuel components include
20 hydrocarbons or other compounds in a particular range of carbon numbers, such as up to about C₂₂ or in the range of about C₁₀ to about C₂₀, are intended to indicate, unless the context clearly indicates the contrary, that these compounds may be distributed substantially throughout the stated range or may represent only a portion/portions of that range.

25 Fuels according to the invention may comprise or be composed substantially of hydrocarbons in the C₁ to C₄ or C₁ to C₅ ranges. In many embodiments, the fuels will be composed predominantly, on a weight basis, of hydrocarbons in a range of at least about C₄ or C₅ and higher, e.g., in a range of about C₅ to about C₂₀, in a range of about C₅ to about C₁₈, and in the ranges of
30 about C₅ to about C₉ and about C₁₀ to about C₂₀.

A preferred form of liquid fuel cell fuel according to either of the foregoing aspects comprises a light Fischer-Tropsch liquid containing at least 77 wt. % normal and iso-paraffins, less than 20% wt. % olefins, less than 9 wt. % alcohols, less than 0.001 wt. % sulfur, and less than 5 wt. % aromatics.

- 5 The fuel, or portions of the fuel, may have been subjected to hydrogenation and/or hydrocracking treatment.

- 10 For example, the invention contemplates fuels prepared by subjecting a Fischer-Tropsch liquid product, which may include hydrocarbons in the range of at least about C₄ or at least about C₅, preferably up to about C₂₈, or higher, by
15 subjecting the hydrocarbons to hydrotreating and/or hydrocracking, and by separating from the product of hydrotreating and/or hydrocracking a fuel or fuel component in a suitable boiling range, for example in the ranges of about C₄ or about C₅ to about C₂₀, in the range of about C₅ to about C₁₈, in the range of about C₅ to about C₉, in the ranges of about C₁₀ to about C₁₈ or about C₂₀, or any other useful range.

According to another aspect of the present invention, a Fischer-Tropsch fuel cell fuel is formed as a blend of one or more alcohols (up to 9 wt. %) and a Fischer-Tropsch product. The alcohols may include methanol, ethanol, propanol, and/or butanol which may be process alcohols, and/or may be from other sources.

- 20 Or the fuel cell fuel may be a blend of Fischer-Tropsch product containing from 70 to more than 99 wt. % normal and iso-paraffin, less than 20% wt. % olefins, less than 0.001 wt. % sulfur, less than 5% wt. % aromatics and up to about 9 wt. %, based on the total weight of blend, of alcohol or alcohols comprising at least one member of the group consisting of methanol, ethanol,
25 propanol and butanol.

- 30 In another embodiment of the second aspect of the invention, the fuel-cell fuel may be a light Fischer-Tropsch liquid having: at least about 20, more particularly at least about 50, preferably at least about 77 and more preferably at least about 95 wt. % of normal and/or iso-paraffins; less than about 70, more particularly less than about 50, preferably less than about 35 and more preferably

less than about 20 wt. % olefins; less than 5 or less than 1 wt. % aromatics; less than 9, more particularly less than 5, preferably less than 1 and more preferably less than 0.1 wt. % alcohols; preferably less than 0.001, more preferably less than 0.0005 and still more preferably less than 0.0001 wt. % sulfur; and preferably less than 0.050, more preferably less than 0.010, still more preferably less than 0.001 and yet more preferably less than 0.0005 wt. % nitrogen.

In yet another aspect, the fuel cell fuel may be composed predominantly, on a weight basis, of material in the C₉-C₂₂ range, and include material boiling above and below 700 degrees F. At least about 50% by weight of the material boiling above 700 degrees F. has been subjected to treatment with hydrogen under conditions sufficient to saturate at least a portion of any aromatics and/or other unsaturates that may have been present therein. Moreover, the fuel comprises at least about 99, at least about 99.3 or at least about 99.5% by weight of normal- and/or iso- paraffins based on the total weight of hydrocarbons, and has less than about 500, or less than about 200, or less than about 100, or less than about 50, or substantially zero ppm of unsaturates, based on the total weight of said fuel. The latter also has a cetane number of at least about 70, at least about 74 or at least about 75, and contains less than about 1 ppm, less than about 750 ppb, less than about 500 ppb or less than about 300 ppb each of S and N, based on the total weight of the fuel.

According to a preferred embodiment, the fuel hydrocarbon content is composed predominantly, or substantially, or entirely of material prepared by Fischer-Tropsch synthesis.

In still another embodiment, the hydrocarbon content of the fuel has an iso- to normal- paraffin weight ratio in the range about 0.02:1 to about 20:1, or in the range of about 0.1:1 to about 15:1, or in the range of about 0.5:1 to about 12:1.

In other embodiments, (a) at least about 50% by weight of the material boiling below 700 degrees F., or (b) substantially all of the material boiling above 700 degrees F., or (c) substantially all of the material boiling below 700 degrees F., or any combination thereof, has been subjected to treatment with hydrogen under conditions sufficient to saturate at least a portion, a substantial portion, or

substantially all, of any aromatics and/or other unsaturates that may have been present therein.

5 In still another embodiment, the fuel is composed predominantly, or substantially, or entirely of material prepared by Fischer-Tropsch synthesis, and substantially all of the material prepared by Fischer-Tropsch synthesis has been subjected to treatment with hydrogen under conditions sufficient to saturate at least a portion, a substantial portion, or substantially all, of any unsaturates and/or alcohols that may have been present therein.

10 In particularly preferred embodiments, the fuel contains less than about 200, less than about 100, less than about 50 or substantially zero ppm of C₁₂-C₂₄ primary alcohol oxygenate, as oxygen, on a water free basis, based on the total weight of said fuel.

15 There are also embodiments of the invention in which the fuel has a flash point, as measured by ASTM D-93 of at least about 80 degrees F., or at least about 100 degrees F., or at least about 120 degrees F, or at least about 150 degrees F.

In other embodiments, the fuel has a flash point, as measured by ASTM D-93, in the range of about 80 to about 150 degrees F., or in the range of about 90 to about 130 degrees F.

20 Another aspect of the invention is a method of manufacturing a fuel cell fuel comprising: preparing a Fischer-Tropsch product; separating from the Fischer-Tropsch product a light portion comprising material in the range of C₅ to C₂₀ or C₂₈ having at least 77 wt. % normal and iso-paraffins, less than 20 wt. % olefins, less than 9 wt. % alcohols, less than 0.001 wt. % sulfur, and less than 5
25 wt. % aromatics.

The invention also includes certain improvements representing preferred embodiments of the foregoing general method. In one such embodiment, the step of separating comprises separating from the Fischer-Tropsch product a light Fischer-Tropsch liquid having less than 1 wt. % aromatics.

Another embodiment of the method of manufacturing a fuel-cell fuel further comprises the step of hydrogenating the light portion.

According to another embodiment of this method of manufacturing a fuel-cell fuel, the separated light portion makes up the fuel cell fuel.

5 Yet another embodiment of this method further comprises: separating from the Fischer-Tropsch product a heavy portion comprising material in the range of C_{21+} ; hydrocracking the heavy portion to produce a hydrocrackate; and separating material in the range of C_5 to C_{20} from the hydrocrackate.

10 In one optional way of performing the last-mentioned embodiment, the material in the range of C_5 to C_{20} separated from the hydrocrackate makes up the fuel cell fuel.

Another optional way of performing the method of manufacturing a fuel-cell fuel and various embodiments thereof comprises the step of hydrogenating the light product stream.

15 In other optional ways of performing the method of manufacturing a fuel-cell fuel and various embodiments thereof, the hydrocrackate and the hydrogenated light portion make up the fuel cell fuel.

20 According to a preferred embodiment of the foregoing method, the separated light Fischer-Tropsch liquid comprises a fuel additive; and said fuel additive is added to a petroleum fuel feedstock to provide a product with less than about 0.05 wt. % sulfur and less than about 10 wt. % aromatics, and wherein the resultant product comprises the fuel-cell fuel.

25 Any of the above-described fuels may be used as the sole fuels or as blends containing these fuels and one or more other fuel component(s), such as alcohols or petroleum-based fuels, in fuel cell systems and in systems powered by fuel cells.

Thus, yet another aspect of the invention comprises a fuel cell system, as above described, containing any of the above-described fuels according to the invention, whether as the sole fuel or as an additive to or blend with another fuel component(s).

5 Moreover, the invention includes fuel cell powered systems, such as aerial, marine or land vehicles or homes or businesses containing appliances, i.e., heating or cooling units or other devices, that are electrically inter-connected with a fuel cell system containing a fuel according to the invention.

10 A specific example of a fuel cell powered system according to the invention is a conversion system for converting light hydrocarbons into heavier hydrocarbons. It includes: a synthesis gas subsystem for receiving light hydrocarbons and, optionally, other synthesis gas forming reactants, such as steam and/or oxygen-containing gas, and for developing a synthesis gas therefrom; a synthesis subsystem fluidly coupled to the synthesis gas subsystem
15 for receiving synthesis gas therefrom and producing heavier hydrocarbons therefrom; a fuel cell processor fluidly coupled to the synthesis gas subsystem for receiving synthesis gas therefrom and preparing the synthesis gas for use in a fuel cell as a hydrogen-containing gas; and a fuel cell coupled to the fuel-cell processor for receiving a hydrogen-containing gas therefrom and producing
20 electrical power. The electrical power may be fed to power-consuming devices, such as lighting, heating and pumping or compressing facilities, within or without the hydrocarbon conversion system.

 According to a preferred form of the specific example of the invention described in the preceding paragraph, the synthesis subsystem is adapted to
25 produce heavier hydrocarbons and tail gas and the fuel cell processor is adapted to prepare the tail gas for use as a hydrogen-containing gas in the fuel cell to produce electrical power.

 According to yet another aspect of the present invention, a conversion system for converting light hydrocarbons into heavier hydrocarbons includes a fuel
30 cell system for receiving light hydrocarbons and, optionally, other synthesis gas forming reactants, such as steam and/or oxygen-containing gas, for generating a

first synthesis gas and electrical power; and a synthesis unit coupled to the fuel cell for receiving a first synthesis gas therefrom and generating the heavier hydrocarbons therefrom.

5 In a preferred embodiment, the conversion system of the foregoing aspect further comprises a synthesis gas unit operable to produce a second synthesis gas, the synthesis gas unit being fluidly coupled to the synthesis unit.

10 Another aspect of the invention is a method of operating a fuel cell to produce electrical power. Thus, in one embodiment, the invention includes a method which comprises the steps of: providing a fuel cell fuel that may comprise or may be composed substantially of synthetic products of Fischer-Tropsch processing, including paraffinic and optionally iso-paraffinic hydrocarbons, and containing less than 0.001 weight percent of sulfur; and supplying the fuel cell fuel to the fuel cell to produce electrical energy therefrom.

15 In another embodiment of this aspect, the method of operating a fuel cell to produce electrical power comprises the steps of: providing a fuel cell fuel that may comprise or be substantially composed of synthetic liquid, gaseous and/or vaporous products, preferably predominantly by weight liquid products, of Fischer-Tropsch processing, which have optionally been hydroisomerized and/or hydrocracked, including paraffinic and optionally iso-paraffinic hydrocarbons,
20 having up to about 18, up to about 20 or up to about 22 carbon atoms.

In another embodiment, the fuel cell operating method comprises the steps of: providing a fuel cell fuel comprising a light Fischer-Tropsch liquid having at least 77 wt. % normal and iso-paraffins, less than 20 wt. % olefins, less than 9 wt. % alcohols, less than 0.001 wt. % sulfur, and less than 5 wt. % aromatics; and
25 supplying the fuel-cell fuel to the fuel cell to produce electrical energy therefrom.

Any of the embodiments of these methods of operating a fuel cell may further comprise the step of providing a fuel cell fuel containing less than 5 or less than 1 weight percent of aromatics.

Moreover, the foregoing methods of operating a fuel cell may include the use of a fuel cell fuel which is a blend of said light Fischer-Tropsch liquid containing from 70 to more than 99 wt. % normal and iso-paraffins, less than 20 wt. % olefins, less than 0.001 wt. % sulfur, less than 5 wt. % aromatics and up to about 9 wt. %, based on the total weight of blend, of alcohol or alcohols comprising at least one member of the group consisting of methanol, ethanol, propanol and butanol.

ADVANTAGES

Although all of the embodiments included within the scope of the invention will not possess all of the following advantages, certain preferred embodiments of the invention will be found to exhibit one or more of these advantages.

The preferred fuel cell fuels based on Fischer-Tropsch liquids provide, on a per unit fuel volume basis, high yields of hydrogen from a fuel cell fuel processor. It will be shown to what extent certain preferred embodiments of the Fischer-Tropsch based fuel cell fuels can provide greater energy density than other fuel cell fuels, such as methane and methanol. It appears that the theoretical hydrogen yield of C₅-C₉ F-T fuel cell fuel is approximately 90 % greater, by volume, and approximately 110% greater, by mass, than that of methanol.

It appears that a fuel cell power generation station, or buses using synthetic gasoline-range paraffin, could generate greater than 87% more energy from a given volume of fuel than from the same fuel cell using methanol, based on non-ideal conversion to H₂ and CO. Vehicles using such a fuel could travel almost twice as far as the same vehicle using methanol or methane.

Certain embodiments of the fuel-cell fuel can readily be handled in the same fuel distribution systems used for distributing and dispensing internal combustion engine fuels such as gasoline and diesel fuel. Thus, refueling would be no more complicated than fueling a car today, and would involve none of the toxicity concerns of methanol

With a fuel cell fuel from the Fischer-Tropsch process as described herein, that contains substantially no sulfur, no or minimal aromatics, and only small amounts of olefins and alcohol, many of the present complications of gasoline reforming for fuel cells are eliminated. Fuel cell fuel processor systems no longer
5 need to scrub sulfur, chlorine, and metal from the processor gas stream. The task of removing sulfur from the hydrogen feed stream before it can damage the fuel cell is all but eliminated. Implications of a clean, substantially sulfur-free fuel cell fuel with no or minimal aromatics are interesting.

F-T (Fischer-Tropsch)-alcohol fuel cell fuel blends in which paraffins are
10 replaced by alcohol(s) of equivalent or lesser carbon number have lower pour-point temperatures than those of F-T neat. This is due to the presence of the alcohol or alcohols in the blends. Thus, such blends may have lower start-up temperatures in the presence of some catalysts. These blends also have a
hydrogen carrying capacity which is higher than that of pure alcohol or alcohol fuel
15 cell fuel blends and proportional to the F-T component of the F-T-alcohol blend fuel cell fuel.

Another advantage is that the fuel-cell fuel can be made from feedstock natural gas generally available worldwide.

Still another advantage is that including a fuel cell as an aspect of a
20 conversion system for converting light hydrocarbons to heavier hydrocarbons can result in improved system efficiency.

BRIEF DESCRIPTION OF THE DRAWINGS

The accompanying drawings, which are illustrative and non-limiting, include illustrations of embodiments of the invention and its advantages.

25 FIGURE 1 is a schematic diagram of a system for converting light hydrocarbons into heavier hydrocarbons, including a fuel-cell fuel.

FIGURE 2 is a bar chart, based on theoretical calculations, showing the relative hydrogen yields of a number of species, including an embodiment of the present invention.

5 FIGURE 3 is a schematic diagram of a conversion system for converting lighter hydrocarbons into heavier hydrocarbons according to the invention.

FIGURE 4 is a schematic diagram of another example of a conversion system for converting lighter hydrocarbons into heavier hydrocarbons according to an aspect of the present invention.

10 FIGURE 5 is a schematic diagram of yet another conversion system for converting lighter hydrocarbons into heavier hydrocarbons in which a fuel cell is used at least in part to produce synthesis gas.

FIGURE 6 is a schematic diagram of a system for hydrogenating a portion of the F-T product stream.

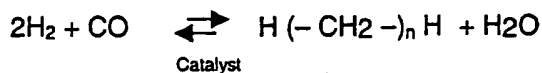
15 FIGURE 7 is a schematic diagram of a system for hydrocracking all of the F-T product.

DESCRIPTION OF VARIOUS AND PREFERRED EMBODIMENTS

20 For a more complete understanding of the present invention and advantages thereof, reference is now made to the following description of various illustrative and non-limiting embodiments thereof, taken in conjunction with the accompanying drawings in which like reference numbers indicate like features.

A. Introduction to The Fischer-Tropsch Process

The Fischer-Tropsch reaction for converting synthesis gas, which is usually primarily CO and H₂, has been characterized in some instances by the following general reaction:



The hydrocarbon products derived from the Fischer-Tropsch reaction range from some methane to high molecular weight paraffin waxes containing more than 50 carbon atoms ($n = 1-50$). Both normal- and iso- paraffins, including both saturated and unsaturated hydrocarbons, and some aromatics and alcohols, may be produced. In practice, the mole ratio of H_2 and CO used to conduct the reaction varies. It has been suggested that this ratio can vary from about 1:1 to about 3:1 (H_2/CO). The synthesis reaction is exothermic and temperature sensitive whereby temperature control is required to maintain desired hydrocarbon product selectivity.

Numerous catalysts have been used in carrying out the Fischer-Tropsch reaction, such as iron-, cobalt-, rhenium- or ruthenium- based catalysts. Cobalt-based catalysts, supported on an alumina or other suitable support, are preferred for use in the present invention.

Operating conditions that minimize formation of carbon dioxide byproducts are preferred. Thus, non-shift Fischer-Tropsch reaction conditions are preferred, and these can be achieved by a variety of methods, including one or more of the following: operating at relatively low carbon monoxide partial pressures, that is, operating at hydrogen to carbon monoxide ratios of at least about 1.4:1 to about 2.5:1, more particularly about 1.7 to about 2.5:1, more particularly at least about 1.9:1 and still more particularly in the range of about 1.9:1 to about 2.3:1 for a cobalt-based catalyst. Operating with ratios below 2:1 may be of assistance in minimizing water deactivation of cobalt-based catalysts. Optimum ratios for other F-T catalysts may vary.

B. Synthesis Gas Production

Synthesis gas may be made from natural gas, gasified coal, and other gaseous raw materials. Three basic methods have been most frequently mentioned as useful for producing the synthesis gas ("syngas"), which is substantially carbon monoxide and molecular hydrogen, utilized as feedstock in the Fischer-Tropsch reaction. These include steam reforming, partial oxidation or

autothermal reforming. For example, see U.S. Patent 2,552,308. However, it has been suggested that relatively low temperature plasma (high voltage ionization field) treatment of light hydrocarbons, with or without some oxygen present, is also useful for making synthesis gas. An autothermal reformer utilizes steam with
5 O.C.G. (oxygen-containing gas), for example air, enriched air, or oxygen. The autothermal reforming process can be carried out in a relatively inexpensive refractory lined carbon steel vessel whereby a lower relative cost is typically involved.

The autothermal process results in lower hydrogen to carbon monoxide
10 ratio in the synthesis gas than does steam reforming alone. That is, the steam reforming reaction with methane results in a ratio of about 3:1 or higher while the partial oxidation of methane results in a ratio of less than about 2:1. A good ratio for the hydrocarbon synthesis reaction carried out at low or medium pressure over a cobalt catalyst is about 2:1 or less, such as about 1.9. When the feed to the
15 autothermal reforming process is a mixture of light shorter-chain hydrocarbons such as a natural gas stream, some form of additional control may be required if it is desired to maintain the ratio of hydrogen to carbon monoxide in the synthesis gas at a ratio of about 2:1. For this reason steam and/or CO₂ may be added to the synthesis gas reactor. See for example, United States Patents 4,883,170 to
20 Agee and 4,973,453 to Agee, which are both incorporated by reference herein for all purposes.

C. ILLUSTRATIVE CONVERSION SYSTEM FOR PRODUCING FUEL-CELL FUELS

Referring now to FIGURE 1, an example of a Fischer-Tropsch system is
25 presented. Conversion system 110 is preferably a Fischer-Tropsch system for converting lighter, shorter-chain hydrocarbons to heavier, longer-chain hydrocarbons. System 110 has a synthesis gas system, in this case synthesis gas subsystem 112, and a synthesis subsystem 116. The synthesis gas subsystem 112 receives a plurality of feedstocks and produces synthesis gas,
30 which includes primarily hydrogen and carbon monoxide. The synthesis gas is delivered to a synthesis subsystem 116 where heavier, longer-chain hydrocarbons are formed. As will be described further below, one or more of the plurality of

feedstocks may be enriched with respect to carbon through a stripper (or contaminant removal) subsystem 114. The stripper subsystem 114 strips or helps to remove contaminants from one or more byproduct water streams delivered to it from the synthesis gas subsystem 112 and/or the synthesis subsystem 116.

5 The plurality of feed streams to the synthesis gas subsystem 112 may include an O.C.G., oxygen-containing gas, such as air or enriched air, which is shown delivered through conduit 118; steam, which is shown delivered through conduit 120; a low-BTU residue, or tail gas, which is delivered through conduit 122; and light hydrocarbons, which are shown delivered through conduits 123 and
10 124. The hydrocarbon feedstock delivered through conduits 123 and 124 is a hydrocarbon feedstock that has been carbon enriched by stripper subsystem 114. The synthesis gas prepared by synthesis gas subsystem 112 is delivered through synthesis gas conduit 126 to synthesis subsystem 116.

 Synthesis gas subsystem 112 may utilize a partial oxidation system, a
15 steam reformer, an autothermal reformer, or a plasma syngas generator, using air, enriched air, oxygen, or other oxygen-containing gas or gases. By "enriched air," is meant air, the oxygen content of which has been increased to above that of standard air, i.e., above about 21 percent oxygen.

 Synthesis subsystem 116 receives synthesis gas from subsystem 112 and
20 uses a reactor or reactors with a catalyst to produce heavier, longer-chain hydrocarbons preferably using the Fischer-Tropsch reaction. Any suitable Fischer-Tropsch catalyst may be used. The catalysts include cobalt or iron as the primary catalysts, preferably supported cobalt, and more preferably supported cobalt where the support may be silica, alumina, silica-alumina or Group IVB metal
25 oxides, e.g. titania. Promoters may also be employed, e.g. ruthenium, rhenium, titanium, zirconium, hafnium. Whereas various catalysts can be used to convert synthesis gas to Fischer-Tropsch liquids, supported cobalt catalysts are preferred in that they tend to produce primarily paraffinic product.

 The synthesis subsystem 116 produces a heavy Fischer-Tropsch liquid and
30 light Fischer-Tropsch liquid that are separated. The heavy Fischer-Tropsch liquid is delivered into conduit 128 where it may go to storage or to be hydrocracked and

then go to stabilization or directly to storage. The light Fischer-Tropsch liquid (preferably about C₄ to about C₂₈) is delivered into conduit 130, from where it may proceed to storage or on for other processing or use. The light Fischer-Tropsch liquid is essentially a flash product that has been flashed at temperature and pressure such that the liquid contains a broad boiling range, about C₄ to about C₂₈ with a bell-curve type distribution. The light Fischer-Tropsch liquid will substantially overlap the heavy Fischer-Tropsch liquid. At room temperature, the light Fischer-Tropsch liquid is a liquid and the heavy Fischer-Tropsch liquid is a solid.

A low BTU residual gas or tail gas (substantially C₅ or less) is separated from the light F-T liquid product stream and delivered into conduit 122. The residual or tail gas delivered into conduit 122 may be returned to the synthesis gas subsystem 112, where it may be used as a fuel for a combustor of a turbine, as fuel for burners used within subsystem 112, or for other useful purposes.

Synthesis subsystem 116 also produces process condensate stream or byproduct water that is delivered into conduit 132, which delivers the aqueous byproduct to stripper subsystem 114. Synthesis gas subsystem 112 also produces process condensate stream or byproduct water, which is also carried to stripper subsystem 114 by a conduit 134. The synthesis subsystem 116, which preferably includes a Fischer-Tropsch reactor, produces aqueous byproducts. As noted earlier, the synthesis gas subsystem 112, which includes an autothermal reformer, produces aqueous byproducts that include contaminants such as ammonia and other nitrogen species.

Before the aqueous byproduct streams from subsystems 112 and 116 may be disposed of or utilized elsewhere in the process, contaminants should be substantially removed or lowered to safe levels, and for this reason, a stripper subsystem 114 is included as an important aspect of the present invention. The treated water from which the contaminants have been substantially removed by stripper subsystem 114 is delivered to conduit 138. The process alcohols in conduit 124 stripped from byproduct streams 132 and/or 138 may be separated and blended with fuel-cell fuels produced from the product streams of 130 and/or 128, if desired. The process alcohols are produced during production of the F-T

liquids. For example, the product water from the F-T reactor may include methanol and ethanol that can be captured and reintroduced to form a fuel-cell fuel. Up to 9 wt. % alcohol is the preferred range.

From there the treated water may be delivered to other parts of system 110, such as for use as boiler feed water in a closed loop cooling system associated with either a reactor in synthesis gas subsystem 112 or a reactor, such as the Fischer-Tropsch reactor, of synthesis subsystem 116. Other Fischer-Tropsch systems may be used as well to produce the fuel-cell fuel described herein; for example, the systems shown in U.S. Patent 5,733, 941 or U.S. Pat. 5,861,441, both of which are incorporated by reference for all purposes, might be used.

The light F-T liquid product delivered to conduit 130 may be further separated as necessary to produce a product in the range of from about C₄ or C₅ to about C₁₈ or to about C₂₀ or to about C₂₂, or in the range of about C₁₀ to about C₂₀ or preferably in the range of about C₅ to about C₉, having the following characteristics: at least 77 wt. % normal and iso-paraffins, less than 20 wt. % olefins, less than 9 wt. % alcohols, less than 0.001 wt. % sulfur, and less than 10 wt. % aromatics (preferably less than 5 wt. % aromatics, and more preferably still less than 1 wt. % aromatics). As such, the product makes a good fuel-cell fuel.

The fuel based on F-T light liquid product may be further hydroprocessed (saturated with hydrogen) if desired. In addition, the heavy F-T product of conduit 128 may be hydrocracked to a hydrocrackate in the range of from about C₄ or C₅ to about C₁₈ or to about C₂₀ or to about C₂₂, or in the range of about C₁₀ to about C₂₀ or preferably in the range of about C₅ to about C₉, which is useful as fuel cell fuel. The hydrocracking may include hydrotreating to reduce or remove unsaturation in the hydrocrackate.

What has been referred to as the fuel-cell fuel above may be used as an additive or intermediate product to mix with conventional petroleum fuels, such as diesel, gasoline, jet fuels, etc., to arrive at a resultant fuel-cell fuel that has less than .05 wt. % sulfur and less than 10 wt. % aromatics. Other additives might be added as well.

The following chart shows calculated theoretical hydrogen yields for Fischer-Tropsch based fuels and other fuels processed in a fuel cell fuel processor.

5	Fuel	Formula	H ₂ Yield (Max)		CO ₂ Yield (Min.)	
			<u>Kg/L</u>	<u>Kg/kg</u>	<u>Kg/L</u>	<u>Kg/kg</u>
	Methanol	CH ₃ OH	0.125	0.159	1.08	1.38
	Ethanol	C ₂ H ₅ OH	0.159	0.204	1.47	1.87
	Gasoline	C _{7.3} H _{14.8} O _{0.1}	0.224	0.321	2.16	3.09
10	F-T Fuel (one embodiment)	C _{7.01} H _{15.9}	0.235	0.336	2.16	3.08

Kg/L = kg of H₂ per Liter of fuel; kg/kg = kg of H₂ per kg of fuel.

Compared to methanol, the F-T-based fuel can produce about 90 % more hydrogen based on fuel volume and 111 % more hydrogen based on fuel weight, after the water gas shift reaction in a fuel cell fuel processor.

The bar graph of Figure 2 illustrates comparative H₂ yields achievable from reforming the species indicated therein, assuming complete conversion of equivalent volumes of those species to CO₂ and H₂. These relative yields assume complete water gas shift reaction. That reaction is defined as $n \text{ C} + 2n \text{ H}_2\text{O} \rightarrow n \text{ CO}_2 + 2n \text{ H}_2$.

Other systems and fuel cell fuels are discussed further below.

D. FUEL CELL ENHANCED FISCHER-TROPSCH SYSTEM

While Fischer-Tropsch derived fuel affords significant advantages to fuel cells, advantages may also be obtained in a Fischer-Tropsch system by incorporating one or more fuel cells. Referring to FIGURE 3, a fuel cell enhanced conversion system 200 is presented. System 200 is in most respects a Fischer-Tropsch conversion system similar to that shown in FIGURE 1, except a fuel cell

202 has been added to use a portion of the synthesis gas to generate electricity that may be used elsewhere in the plant such as to assist with compression.

Light hydrocarbons 204 are delivered to a synthesis gas subsystem 206, which may be a partial oxidation system, steam reformer, autothermal reformer, or plasma type syngas generator. Steam 208, which may be used to adjust the molar ratios of the syngas, and oxygen-containing gas 210 are also delivered to the synthesis gas subsystem 206. The synthesis gas subsystem 206 produces synthesis gas 212 (substantially CO and molecular hydrogen) that is delivered to a synthesis subsystem 214, which is preferably a Fischer-Tropsch based system.

The synthesis subsystem 214 produces a heavy product 217 (e.g., C_{14+} , but predominantly C_{18+}) that goes to storage 219, and a lighter product and water that are separated by separator 218. Water 220 can go for treatment and heavier products 222 (preferably C_5-C_{18}) that are separated go to storage 224 or for downstream processing. A light residual gas or tail gas 226 (preferably about C_1-C_5) is delivered to the synthesis gas subsystem 206 for use as fuel in addition to the light hydrocarbons.

A portion of the synthesis gas is delivered to a fuel processor, e.g., water-gas-shift-and-clean-up unit 216, which processes synthesis gas 212 to produce hydrogen for use in the fuel cell 202. For example, unit 216 removes CO, which is a poison to some fuel cell catalysts. Some fuel cell designs perform the processes of unit 216 within the cell.

Fuel cell 202 produces electricity 228 that may be used to drive various components in system 200 and may also be used external to system 200. For example, it is frequently desirable to include an air compressor as part of the synthesis gas subsystem 206 as is suggested by reference numeral 230 (or as part of a pretreatment unit) and the compressor may be powered altogether on in part by electricity 228 from the fuel cell 202.

FIGURE 4 presents another possible embodiment of a fuel cell enhanced conversion system 300 that is analogous to that of FIGURE 3, except the fuel cell fuel processor unit 316 includes a reformer as well as water-gas-shift-and-clean-

up/fuel processor components, and utilizes tail gas 326 from the synthesis subsystem 314. As suggested by conduit 321, unit 316 may also utilize product water 320 for steam generation. Air is delivered through conduit 323. Analogous components have the same last two digits for the reference numerals, but instead of being in the 200s are in the 300s. The tail gas 326 is delivered to a fuel cell fuel processor (water-gas-shift-and-clean-up unit) and then delivered (as a fuel cell fuel of CO₂ and H₂) to the fuel cell 302.

FIGURE 5 presents another embodiment of the present invention with a fuel cell enhanced conversion system that is analogous to FIGURE 4 except that the source of synthesis gas is also a source of electrical power in a Fischer-Tropsch process. The analogous items have corresponding reference numerals. As shown in this embodiment, a system 330 may have a fuel cell 332 as the source of synthesis gas in a Fischer-Tropsch process.

Although the invention can be used with a wide variety of different types of fuel cells, the fuel cell 332 of this embodiment is preferably an internally reforming fuel cell, such as a Solid Oxide Fuel Cell (SOFC), that supplies both power and all or a portion of the synthesis gas for system 330. Fuel 304, steam 308, and an oxygen-containing gas 310 are supplied to the fuel cell 332 where it is converted to electrical power and synthesis gas. Water vapor, tail gas and/or other fuel, and if practical, CO₂ introduced into the SOFC is converted to H₂, H₂O, CO and CO₂. Hydrogen concentration may be controlled by means of pressure swing absorption or other method. CO₂ may be removed for recycle or sequestration. Under appropriate circumstances, a portion of the heat losses linked with the electrochemical production of electrical energy can be used for the reforming process; and the fuel cell stack can be cooled by the endothermic reforming process. Other designs are possible.

The synthesis gas is delivered through conduit 312 to Fischer-Tropsch synthesis unit 314. Power is delivered to power conduit 334 from where it may go to supply power for system 330 as suggested by 336 and/or for external power as suggested by 338.

As one alternative, system 330 may further include a second source of synthesis gas, such as synthesis gas unit 340 shown in dashed lines. Unit 340 may be, for example, an autothermal reformer (ATR) or a partial oxidation unit (POX). If this alternative is used, the additional synthesis gas is delivered through conduit 342 to conduit 312.

5. ADDITIONAL ILLUSTRATIVE FUEL CELL FUEL SYSTEMS

The fuel cell fuel is preferably made through a Fischer-Tropsch system as previously mentioned. Numerous embodiments are possible, and a couple of additional systems are now presented. In one embodiment, substantially the entire F-T light liquid product is hydrogenated to make a saturated stream right away. It can for example contain hydrocarbons in the range of from about C₄ or C₅ to about C₁₈ or to about C₂₀ or to about C₂₂. Alternatively, portions of the light liquid product may be hydrogenated. These can for example contain hydrocarbons in the range of about C₁₀ to about C₂₀ or preferably in the range of about C₅ to about C₉. Preferably a C₅ to C₂₀ light liquid fraction, and preferably a C₅-C₁₀ portion, is used and preferably has at least 90 wt. % paraffin and less than 10 wt. % alcohol and unsaturates. In another embodiment, the F-T product is separated into light and heavy portions and the heavy portion is hydrocracked and/or hydrotreated and blended with the light portion to produce the fuel cell fuel. Further, as described further below, the F-T product may be blended with alcohols and/or other substances to produce the fuel cell fuel.

Referring now to FIGURE 6, a system 400 for producing a fuel cell fuel is presented. System 400 receives synthesis gas, preferably a nitrogen-diluted synthesis gas from a blown synthesis gas system using an oxygen-containing gas, through feed 402. Stream 402 is preferably a synthesis gas with H₂ and CO in mole ratios within the ranges described above. A diluent is present which consists of N₂, and may further have traces of air-related gases and combustion products. The synthesis gas feed 402 is delivered to Fischer-Tropsch unit 404 that contains a Fischer-Tropsch (F-T) reactor at conditions known to those skilled in the art which will produce paraffinic F-T products.

The light gaseous effluent of the F-T unit 404 is delivered as feed 406 to cooling unit 408. Stream 406 will include gaseous F-T reactor effluent with hydrocarbons synthesized from the synthesis gas in the range of C_1 to C_{28} (or greater) as well as unspent synthesis gas, water, and diluent. Unit 408 cools and removes water from the feed. The removed water is carried away as water stream 410. Stream 410 will also include some alcohols that may be stripped allowing the water to be used elsewhere if desired. The liquid product separated in unit 408 is delivered to flash drum 412 by feed 414. Feed 414 includes F-T light oils that are preferably C_4 - C_{28} paraffins, olefins, and alcohols. The gaseous remains, or tailgas, of cooling unit 408 are discharged as stream 416 which may be used elsewhere in system 400 or may be used in the synthesis gas system or a fuel cell system or other processes as a fuel. Stream 416 includes diluent, H_2 , CO , CH_4 and some minor compounds.

The feed 414 is delivered to flash drum 412 and the flashed light product is delivered as feed 418 to distillation unit 420. Feed 418 is the flashed light product (preferably at about 100 psig at 100-200 degrees Fahrenheit). The gaseous effluent is delivered as discharge 422 for use as a fuel gas stream or for other processes.

The heavy F-T products from F-T unit 404 are delivered as feed 424 to solids separation unit 426. Feed 424 is the F-T effluent preferably in the range of about C_{14} to about C_{60} or greater. Solids filtration may or may not be required. If required, some solids will be rejected from the process or recycled. Removed solids 428 may be recycled to unit 404. The product continues as stream 430 to flash drum 432. Stream 430 is an F-T heavy product that is preferably about C_{14} to about C_{60} or higher paraffins. The gaseous product of drum 432 is delivered as stream 434 for inclusion with stream 414. The heavy product stream 436 is delivered to distillation unit 420. Stream 434 is a flash vapor from the F-T heavy product that is preferably at about 115 psig and in the range of about 300 to 600 degrees Fahrenheit. Stream 436 is the flashed heavy product (preferably about 115 psig and 300-600 degrees Fahrenheit).

Distillation unit 420 produces a plurality of cuts. The following discharge streams are preferred from unit 420. Stream 438 is a C₄ and below stream, e.g., with Butane, etc. Stream 440 is the cut preferably containing a C₅ to C₂₀ fuel cell fuel. The fuel cell fuel preferably has at least about 77% wt. Paraffin (normal paraffin and iso-paraffin), less than 20 % wt. Olefins (predominately terminal), less than 9 % wt. Alcohols (predominately primary alcohols), less than 0.001 % wt. Sulfur, and less than 5 % wt. Aromatics. Stream 444 is a C₂₁₊ heavy stream; it is the heavy oil separated for further processing by wax finishing, fuels hydrocracking, or lubricant isomerization. Steam is supplied as needed through feed 446.

Referring now to FIGURE 7, a subsystem 500 may be used with system 400 of FIGURE 6 to process the C₂₁₊ stream 444 from the distillation unit 420. Within hydrocracker unit 502, the stream 444 is boosted to hydrocracker operation pressures and heated to hydrocracker operation temperatures before being exposed to the hydrocracking and/or hydrotreating catalyst. A makeup hydrogen stream 504 provides the necessary hydrogen for the hydrocracking reaction. Stream 506 is the hydrogen purge. Process water is removed as shown by stream 508. Preferred parameters for the reaction zone of unit 502 are as follows: temperatures between 400-800 degrees Fahrenheit (catalyst average temperature); pressure ranging between 300-1500 psig (total pressure); LHSV ranging from 0.5 to 3.0 h⁻¹; a gas to oil ratio of 1000-10000 SCF/Bbl; and finally with the hydro-treating and/or hydrocracking catalyst being a noble metal or base metal oxide on a zeolite-type support, which is a type known to those skilled in the art to which it pertains.

Reactor effluent is cooled and separated via flashing and then fed as light hydrocrackate 510 and heavy hydrocrackate 512 to a distillation unit 520. Unit 520 preferably operates as a steam-stripped column at or near atmospheric pressures. In one mode, two light products are produced from this distillation column/unit 520. First, a light synthetic paraffin stream 522 that is preferably at least about C₄ or about C₅ to about C₉. Second distillate stream 524 is preferably about C₁₀ to about C₂₀ and may be used as a fuel cell fuel or a fuel for gas turbines or compression ignition engines. Steam is provided as needed at 528. The light ends are removed at stream 530. The bottom stream 526 is recycled

and has under-converted products that are combined with the feed 444 and reprocessed. Recycle operations afford higher yields of middle distillates products than a once through arrangement. In the event that a lighter product slate is desired, the cut point between the synthetic distillate 524 and the under-converted oil of stream 526 can be reduced and reaction temperature increased to yield a lighter product. Also the reaction temperature could be reduced, cut point increased, and a heavier distillate product 524 would result. Streams 522 and 524 are both suitable for use as fuel cell fuel separately or in combination or further in combination with stream 440 (FIG. 6).

As an alternative system to that described above (FIGURES 5 and 6), all of the light or heavy F-T flash products of streams 418 and 436 (FIGURE 6) or the C₅ to C₂₀ fuel cell fuel of stream 440 (FIGURE 6) can be taken to a hydrocracker unit 502 (FIGURE 7). Distillation unit 420 may or may not be used with this process. This would be applicable if a completely saturated (with hydrogen) fuel cell fuel is desired. The operation would otherwise be analogous to that described in connection with FIGURE 7.

F. FUEL CELL FUELS MADE WITH BLENDS

The F-T fuel cell fuel described above may also be made as a blended product. An F-T product may be blended with methanol, ethanol, propanol, butanol, or blends of these alcohols or other fuel species. Also, a fuel cell fuel may be made by adding a F-T product to a conventional petroleum fuel feedstock. Conventional petroleum feed stocks includes gasolines with a C₄ to C₁₁ boiling range of napthenes, aromatics, paraffins, and olefins; heavy naptha or a kerosene (C₈ to C₁₅), and #1 diesel.

With the blends, the alcohols may be "process alcohols", i.e., from an F-T system as described above, or may be from another process. The preferred blends include ethanol and/or methanol and may include a blend preferably having greater than 10 wt. % and going up to as much as 95 wt. % of the fuel cell fuel. The blends help lower the fuel cloud point, pour points and fuel cell-processor activation energy and this may have particular advantages in efforts to adapt fuel cells to make practical fuel cell-powered automobiles. Consider that a

lower activation temperature in the fuel cell processor may allow quicker start times for a fuel cell-powered car.

The ability of the blends to help lower the activation energy required in the fuel cell processor may be seen by considering the following catalytic reforming temperatures of a experimental gas composition:

	Fuel Species	Activation Temperature
		(Deg. Centigrade)
	2-Pentene (Olefin)	670
	Toulene (aromatic)	655
10	Iso-Octane (paraffin)	630
	Ethanol (alcohol)	580
	Methanol (alcohol)	450

The blend may be used as the primary fuel or as a startup fuel which can be replaced after startup by a fuel requiring a higher catalyst temperature for partial oxidation.

With the above referenced ranges and suggestions, many possible blended fuel cell fuels are possible. A few examples follow. A Fischer-Tropsch fuel cell fuel made as a blend of process alcohols and a Fischer-Tropsch product with between >99 and 70% normal and iso-paraffin, less than 20 wt. % olefins, less than 0.001 wt. % sulfur, and less than 5 wt. % aromatics. A Fischer-Tropsch fuel cell fuel made as a blend of methanol and a Fischer-Tropsch product having between >99 and 5% normal and iso-paraffin, less than 20 wt. % olefins, less than 0.001 wt. % sulfur, and less than 5 wt. % aromatics. A Fischer-Tropsch fuel cell fuel made as a blend of ethanol and a Fischer-Tropsch product having between >99 and 5% normal and iso-paraffin, less than 20 wt. % olefins, less than 0.001 wt. % sulfur, and less than 5 wt. % aromatics. A Fischer-Tropsch fuel cell fuel made as a blend of propanol and a Fischer-Tropsch product with between >99 and 5% normal and iso-paraffin, less than 20 wt. % olefins, less than 0.001 wt. % sulfur, and less than 5 wt. % aromatics. A Fischer-Tropsch fuel cell fuel made as a blend of butanol and a Fischer-Tropsch product having between >99 and 5%

normal and iso-paraffin, less than 20 wt. % olefins, less than 0.001 wt. % sulfur, and less than 5 wt. % aromatics.

G. CONCLUSION

5 Although the present invention and its advantages have been described in detail, it should be understood that various changes, substitutions and alterations can be made therein without departing from the spirit and scope of invention as defined by the appended claims. For example, components and systems shown in one embodiment may be included in other embodiments.

WHAT IS CLAIMED IS:

1. A liquid fuel cell fuel comprising synthetic products of Fischer-Tropsch processing, including paraffinic and optionally iso-paraffinic hydrocarbons, and containing less than 0.001 weight percent sulfur.
2. A fuel cell fuel according to claim 1 containing less than 5 weight percent of aromatics.
3. A fuel cell fuel according to claim 1 containing tail gas of substantially C₅ or less.
4. A fuel cell fuel according to claim 1 containing liquids boiling in the range of C₅-C₂₀.
5. A fuel cell fuel according to claim 1 comprising more hydrogen than C₄, preferably C₅ and more preferably C₆ hydrocarbon species, or more hydrogen than gasoline derived from petroleum.
6. A liquid fuel cell fuel comprising synthetic liquid, gaseous and/or vaporous products, preferably predominantly by weight liquid products, of Fischer-Tropsch processing, which have optionally been hydroisomerized and/or hydrocracked, including paraffinic and optionally iso-paraffinic hydrocarbons, having up to about 18, up to about 20 or up to about 22 carbon atoms.
7. A fuel cell fuel according to claim 1 or 6 containing less than 5 weight percent or less than 1 weight percent of aromatics.
8. A fuel cell fuel according to claim 1 or 6 containing small or substantial amounts of alcohols, if any, small or substantial amounts of unsaturates other than aromatics, if any, negligible amounts of S, and, preferably, only negligible amounts of N.
9. A fuel cell fuel according to claim 1 or 6 containing hydrocarbons in the C₁ to C₄ or C₁ to C₅ range.

10. A fuel cell fuel according to claim 1 or 6 composed predominantly, on a weight basis, of hydrocarbons in a range of about C₄ or C₅ and higher, in a range of about C₅ to about C₂₀ or of about C₅ to about C₁₈, or in the ranges of about C₅ to about C₉ and about C₁₀ to about C₂₀.
11. A liquid fuel cell fuel according to claim 1 or 6 comprising a light Fischer-Tropsch liquid containing at least 77 wt. % normal and iso-paraffins, less than 20 wt. % olefins, less than 9 wt. % alcohols, less than 0.001 wt. % sulfur, and less than 5 wt. % aromatics.
12. A fuel cell fuel according to claim 1 or 6 wherein the fuel, or portions of the fuel, has/have been subjected to hydrogenation and/or hydrocracking treatment.
13. A fuel cell fuel according to claim 1 or 6 prepared by subjecting a Fischer-Tropsch liquid product including hydrocarbons in the range of at least about C₄ or at least about C₅, and preferably up to about C₂₈, or higher, to hydrotreating and/or hydrocracking, and separating from the product of
5 hydrotreating and/or hydrocracking a fuel or fuel component in the ranges of about C₄ or about C₅ to about C₂₀, in the range of about C₅ to about C₁₈, in the ranges of about C₅ to about C₉ or about C₁₀, or in the ranges of about C₁₀ to about C₁₈ or about C₂₀.
14. According to another aspect of the present invention, a Fischer-Tropsch fuel cell fuel is formed as a blend of one or more alcohols (up to 9 wt. %) and a Fischer-Tropsch product.
15. A fuel cell fuel according to claim 1 which is a blend comprising Fischer-Tropsch product containing from 70 to more than 99 wt. % normal and iso-paraffins, less than 20 wt. % olefins, less than 0.001 wt. % sulfur, less than 5 wt. % aromatics and up to 9 wt. %, based on the total weight of blend, of alcohol or alcohols comprising at least one member of the group consisting of methanol, ethanol, propanol and butanol.

16. A fuel cell fuel according to claim 6 which is a light Fischer-Tropsch liquid having: at least about 20, more particularly at least about 50, preferably at least about 77 and more preferably at least about 95 wt. % of normal and/or iso-paraffins; less than about 70, more particularly less than about 50, preferably less than about 35 and more preferably less than about 20 wt. % olefins; less than 5 or less than 1 wt. % aromatics; less than 9, more particularly less than 5, preferably less than 1 and more preferably less than 0.1 wt. % alcohols; preferably less than 0.001, more preferably less than 0.0005 and still more preferably less than 0.0001 wt. % sulfur; and preferably less than 0.050, more preferably less than 0.010, still more preferably less than 0.001 and yet more preferably less than 0.0005 wt. % nitrogen.

17. A fuel cell fuel according to claim 6 composed predominantly, on a weight basis, of material in the C₉-C₂₂ range, said hydrocarbons including material boiling above and below 700 degrees F., at least about 50% by weight of the material boiling above 700 degrees F. having been subjected to treatment with hydrogen under conditions sufficient to saturate at least a portion of any aromatics and/or other unsaturates that may have been present therein, said fuel comprising at least about 99, at least about 99.3 or at least about 99.5% by weight of normal- and/or iso- paraffins based on the total weight of hydrocarbons, having less than about 500, less than about 200, less than about 100, less than about 50, or substantially zero ppm of unsaturates, based on the total weight of said fuel, having a cetane number of at least about 70, at least about 74 or at least about 75, and containing less than about 1 ppm, less than about 750 ppb, less than about 500 ppb or less than about 300 ppb each of S and N, based on the total weight of said fuel.

18. A fuel cell fuel according to claim 1, 16 or 17 wherein the fuel hydrocarbon content is composed predominantly, or substantially, or entirely of material prepared by Fischer-Tropsch synthesis.

19. A fuel cell fuel according to claim 1, 16 or 17 wherein the hydrocarbon content of the fuel has an iso- to normal- paraffin weight ratio in the

range about 0.02:1 to about 20:1, or in the range of about 0.1:1 to about 15:1, or in the range of about 0.5:1 to about 12:1.

20. A fuel cell fuel according to claim 1, 16 or 17 wherein (a) at least about 50% by weight of the material boiling below 700 degrees F., or (b) substantially all of the material boiling above 700 degrees F., or (c) substantially all of the material boiling below 700 degrees F., or (d) any combination of (a), (b) and/or (c), has been subjected to treatment with hydrogen under conditions sufficient to saturate at least a portion, a substantial portion, or substantially all, of any aromatics and/or other unsaturates that may have been present therein.

21. A fuel cell fuel according to claim 1, 6 or 17 wherein the fuel is composed predominantly, or substantially, or entirely of material prepared by Fischer-Tropsch synthesis, and substantially all of the material prepared by Fischer-Tropsch synthesis has been subjected to treatment with hydrogen under conditions sufficient to saturate at least a portion, a substantial portion, or substantially all, of any unsaturates and/or alcohols that may have been present therein.

22. A fuel cell fuel according to claim 1, 6 or 17 wherein the fuel contains less than about 200, less than about 100, less than about 50 or substantially zero ppm of C₁₂-C₂₄ primary alcohol oxygenate, as oxygen, on a water free basis, based on the total weight of said fuel.

23. A fuel cell fuel according to claim 1, 6 or 17 wherein the fuel has a flash point, as measured by ASTM D-93 of at least about 80 degrees F., or at least about 100 degrees F., or at least about 120 degrees F, or at least about 150 degrees F.

24. A fuel cell fuel according to claim 1, 6 or 17 wherein the fuel has a flash point, as measured by ASTM D-93, in the range of about 80 to about 150 degrees F., or in the range of about 90 to about 130 degrees F.
25. A method of manufacturing a fuel cell fuel comprising: preparing a Fischer-Tropsch product; separating from the Fischer-Tropsch product a light portion comprising material in the range of C_5 to C_{20} or C_{28} having at least 77 wt. % normal and iso-paraffins, less than 20 wt. % olefins, less than 9 wt. % alcohols, less than 0.001 wt. % sulfur, and less than 5 wt. % aromatics.
26. A method of manufacturing a fuel-cell fuel according to claim 25 wherein the fuel contains less than 1 wt. % aromatics.
27. A method of manufacturing a fuel-cell fuel according to claim 25 further comprising the step of hydrogenating the light portion.
28. A method of manufacturing a fuel-cell fuel according to claim 25 wherein the separated light portion makes up the fuel cell fuel.
29. A method of manufacturing a fuel cell fuel according to claim 25 further comprising: separating from the Fischer-Tropsch product a heavy portion comprising material in the range of C_{21+} ; hydrocracking the heavy portion to produce a hydrocrackate; and separating material in the range of C_5 to C_{20} from the hydrocrackate.
30. A method of manufacturing a fuel-cell fuel according to claim 29 wherein the separated heavy portion makes up the fuel cell fuel.
31. A method of manufacturing a fuel cell fuel according to claim 29 which further comprises the step of hydrogenating the light product stream.

32. A method of manufacturing a fuel-cell fuel according to claim 29 or 31 wherein the hydrocrackate and the hydrogenated light portion make up the fuel cell fuel.
33. A method of manufacturing a fuel-cell fuel according to claim 25 or 29 wherein the fuel cell fuel is mixed with a petroleum fuel feedstock to provide a product with less than about 0.05 wt. % sulfur and less than about 10 wt. % aromatics, and wherein the resultant product comprises the fuel cell fuel.
34. A fuel cell system or a system powered by a fuel cell wherein fuel according to claim 1 is present in said fuel cell system or in said system powered by a fuel cell, as the sole fuel or as a blend containing said fuel and another fuel component.
35. A system powered by a fuel cell according to claim 34 wherein said system powered by a fuel cell is an aerial, marine or land vehicle or a home or business containing appliances that are electrically inter-connected with a fuel cell system containing a fuel according to claim 1 or 6.
36. A conversion system for converting light hydrocarbons into heavier hydrocarbons comprising a synthesis gas subsystem for receiving light hydrocarbons and, optionally, other synthesis gas forming reactants, such as steam and/or oxygen-containing gas, and for developing a synthesis gas therefrom; a synthesis subsystem fluidly coupled to the synthesis gas subsystem for receiving synthesis gas therefrom and producing heavier hydrocarbons therefrom; a fuel cell processor fluidly coupled to the synthesis gas subsystem for receiving synthesis gas therefrom and preparing the synthesis gas for use in a fuel cell as a hydrogen-containing gas; and a fuel cell coupled to the fuel-cell processor for receiving a hydrogen-containing gas therefrom and producing electrical power.

37. A conversion system for converting light hydrocarbons according to claim 36 wherein the synthesis subsystem is adapted to produce heavier hydrocarbons and tail gas, and the fuel cell fuel processor is adapted to prepare the tail gas for use as a hydrogen-containing gas in the fuel cell to produce electrical power.

38. A conversion system for converting light hydrocarbons into heavier hydrocarbons including a fuel cell system for receiving light hydrocarbons and hydrocarbon reforming reactants, such as steam and/or oxygen-containing gas, for generating a first synthesis gas and electrical power; and a synthesis unit coupled to the fuel cell for receiving a first synthesis gas therefrom and generating the heavier hydrocarbons therefrom.

39. A conversion system for converting light hydrocarbons according to claim 38 further comprising a synthesis gas unit operable to produce a second synthesis gas, the synthesis gas unit being fluidly coupled to the synthesis unit.

40. A method of operating a fuel cell to produce electrical power, said method comprising the steps of: providing a fuel-cell fuel comprising synthetic products of Fischer-Tropsch processing, including paraffinic and optionally iso-paraffinic hydrocarbons, and containing less than 0.001 weight percent of sulfur; and supplying the fuel cell fuel to the fuel cell to produce electrical energy therefrom.

41. A method of operating a fuel cell to produce electrical power, said method comprising the steps of: providing a fuel-cell fuel comprising synthetic liquid, gaseous and/or vaporous products, preferably predominantly by weight liquid products, of Fischer-Tropsch processing, which have optionally been hydroisomerized and/or hydrocracked, including paraffinic and optionally iso-paraffinic hydrocarbons, having up to about 18, up to about 20 or up to about 22 carbon atoms.

42. A method of operating a fuel cell to produce electrical power, said method comprising the steps of: providing a fuel-cell fuel comprising a light Fischer-Tropsch liquid having at least 77 wt. % normal and iso-paraffins, less than 20 wt. % olefins, less than 9 wt. % alcohols, less than 0.001 wt. % sulfur, and less than 5 wt. % aromatics; and supplying the fuel-cell fuel to the fuel cell to produce electrical energy therefrom.

43. A method of operating a fuel cell according to claim 42 wherein the step of providing a fuel cell fuel further comprises providing a fuel cell fuel having less than 1 wt. % aromatics.

44. A method of operating a fuel cell according to claim 42 wherein the fuel cell fuel is a blend of said light Fischer-Tropsch liquid containing from 70 to more than 99 wt. % normal and iso-paraffins, less than 20 wt. % olefins, less than 0.001 wt. % sulfur, less than 5 wt. % aromatics and up to about 9 wt. %, based on the total weight of blend, of alcohol or alcohols comprising at least one member of the group consisting of process alcohols, methanol, ethanol, propanol, or butanol.

45. All of the inventions explicitly or inherently disclosed herein.

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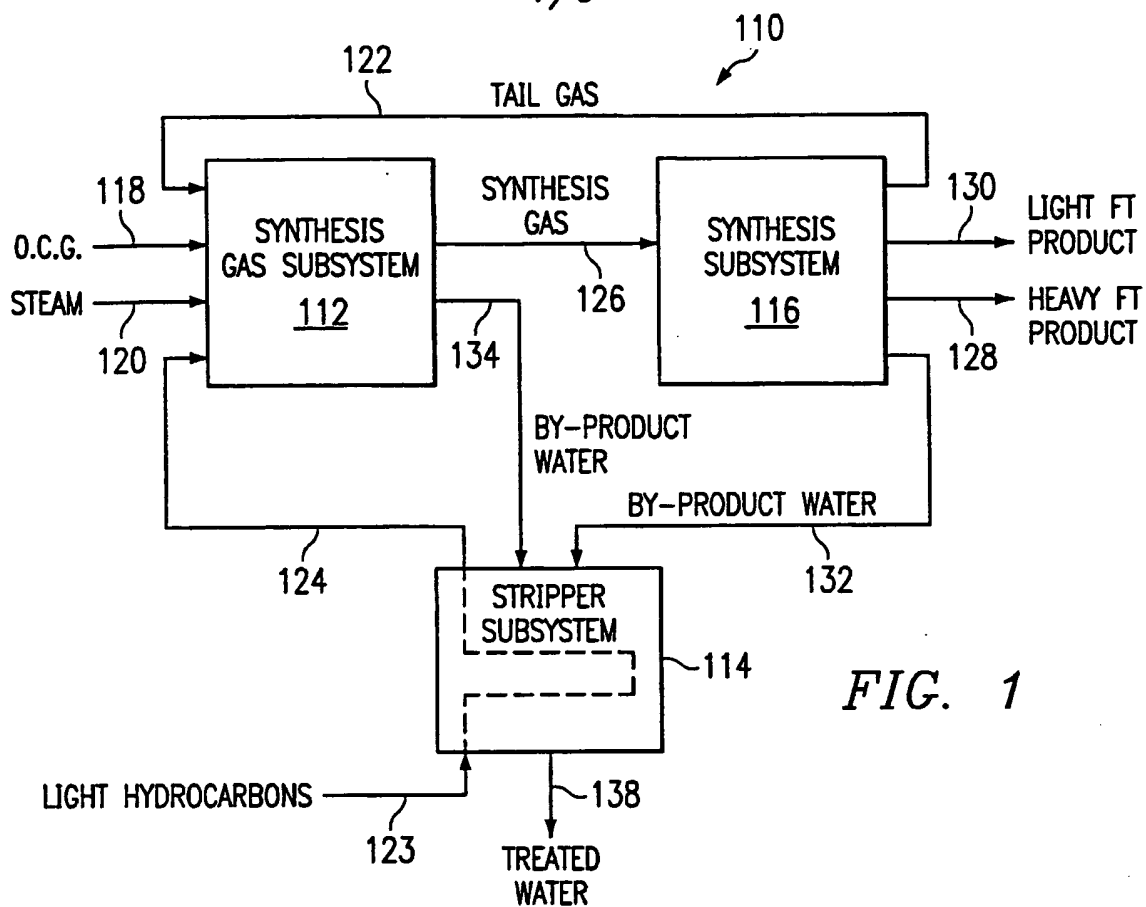
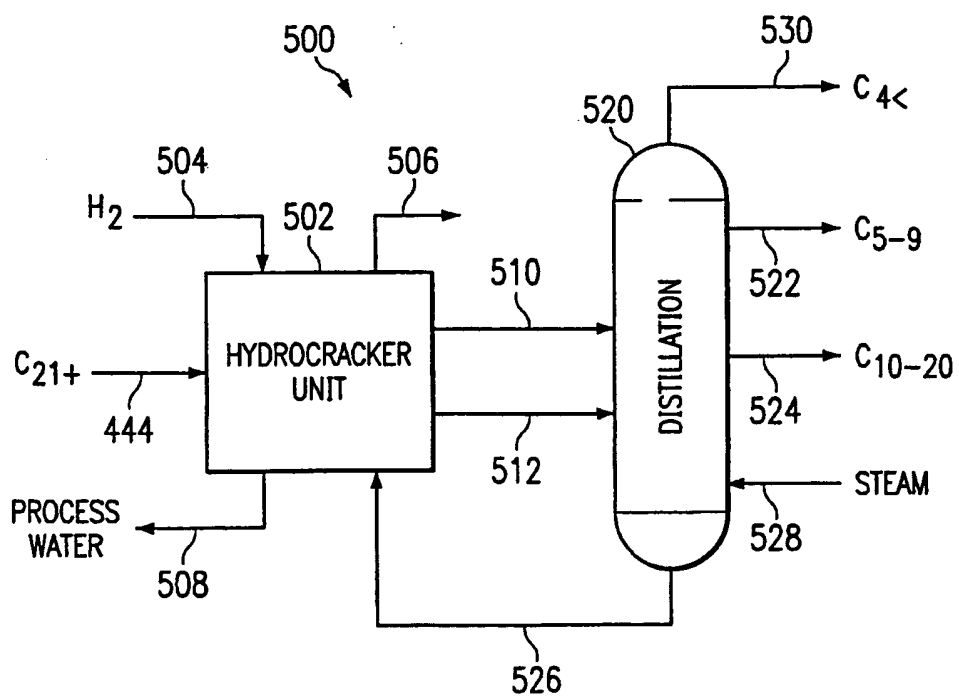


FIG. 7



HYDROGEN TO FUEL CELL PER LITER OF RAW FISCHER-TROPSCH FUEL TO REFORMER (IDEAL CONDITIONS)

WEIGHTED AVERAGE SYNCCELL C5-C9 RAW FT FUEL CELL REFORMER FUEL

KILOGRAMS
H PER
LITER
FUEL

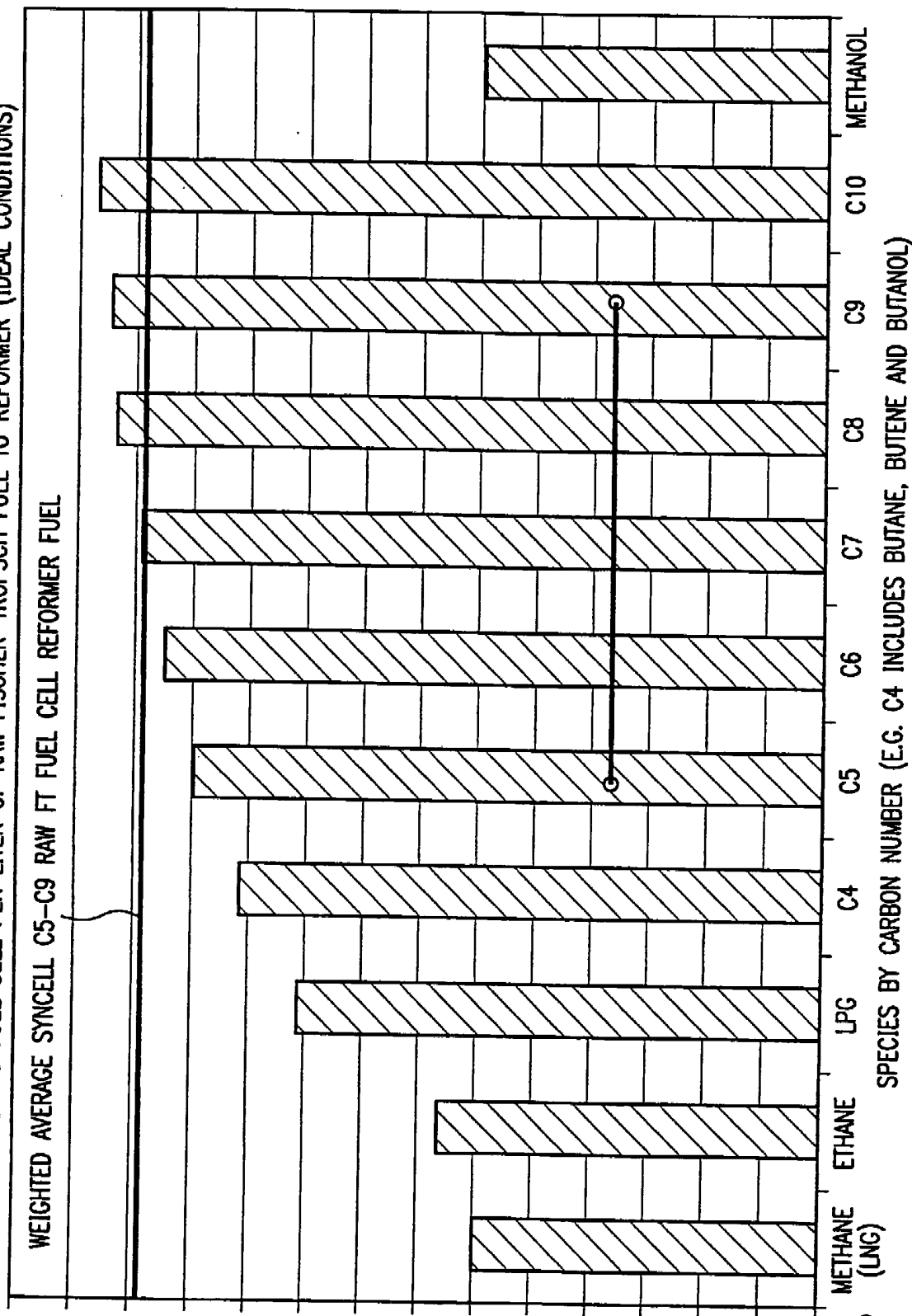
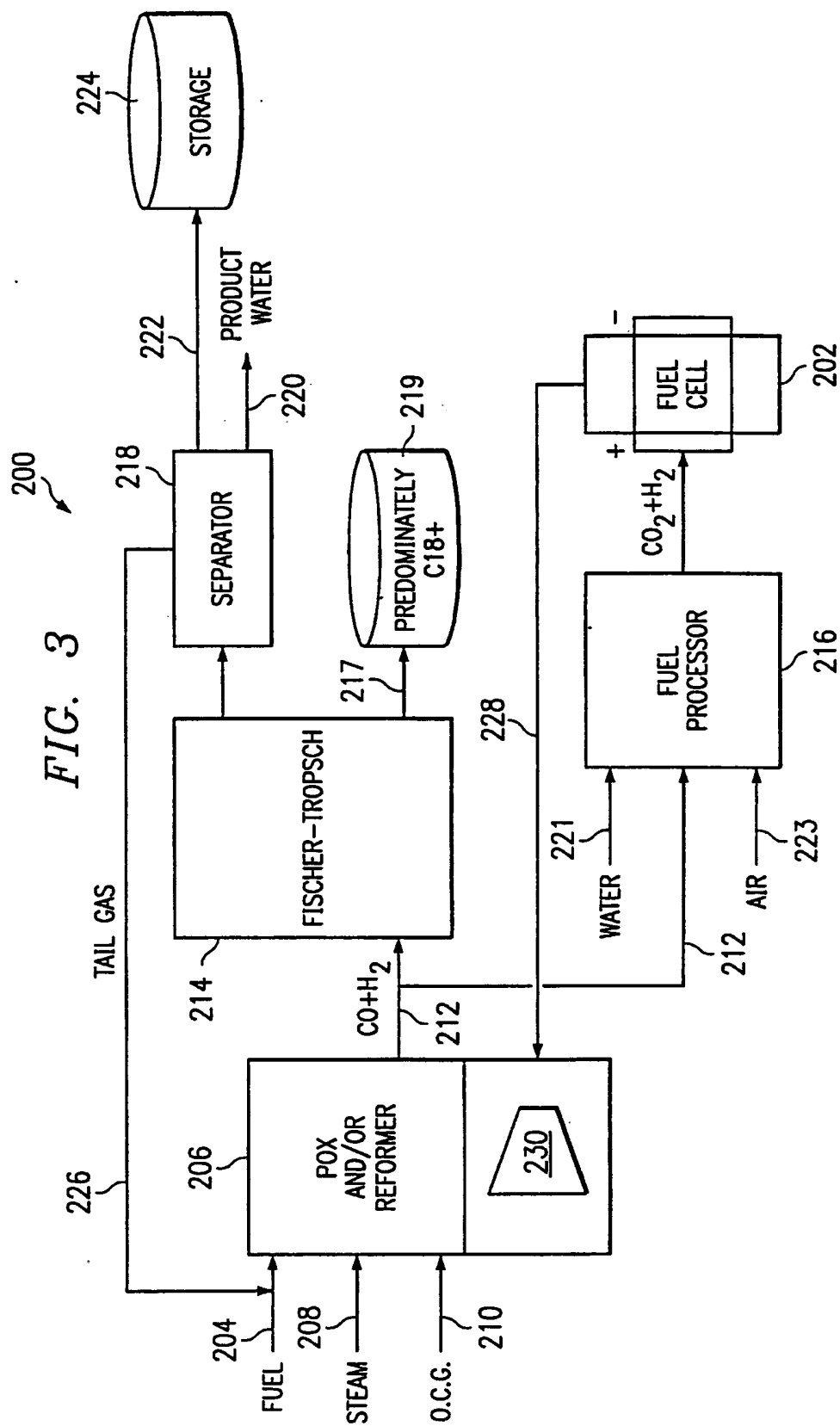
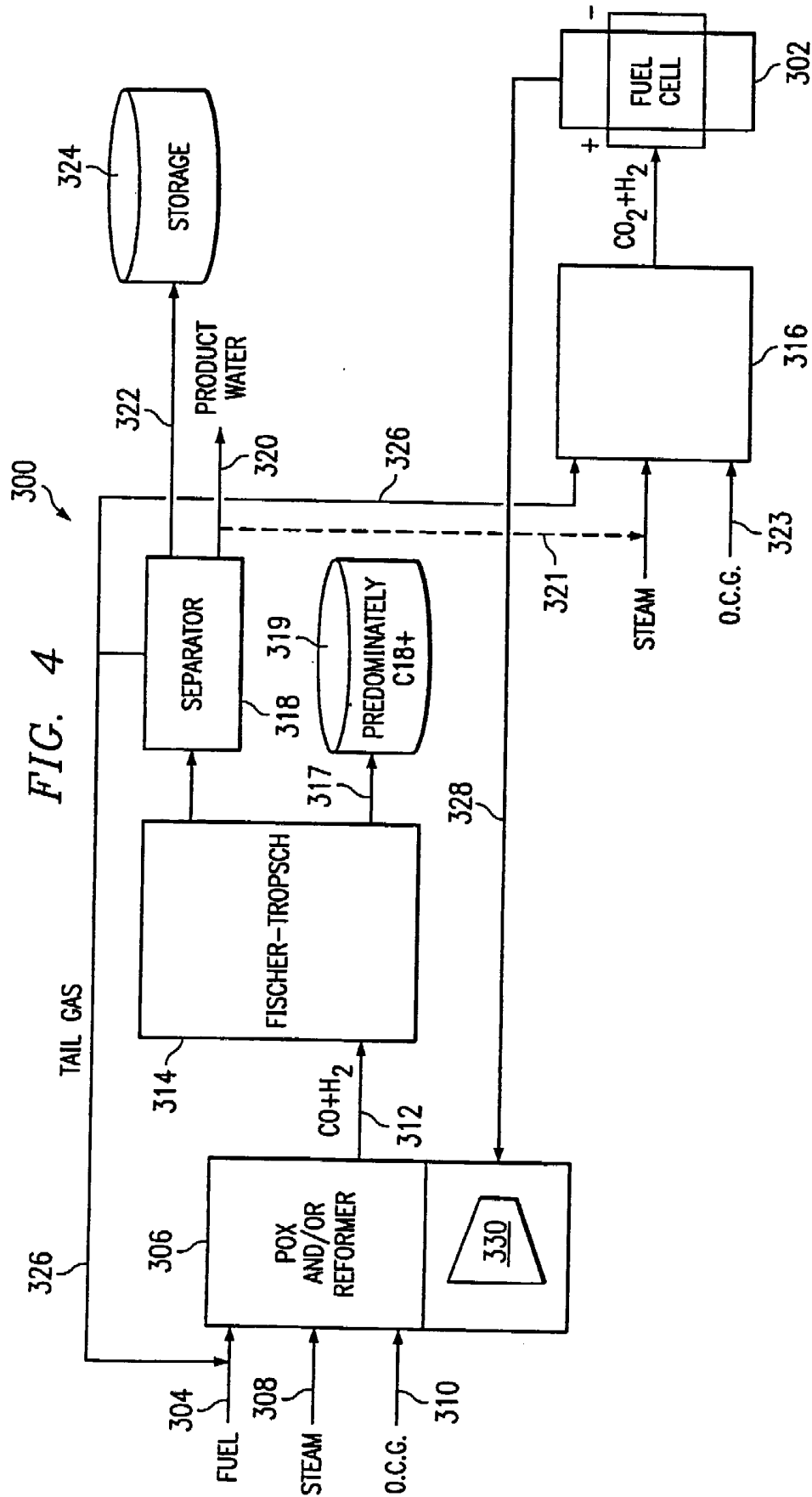
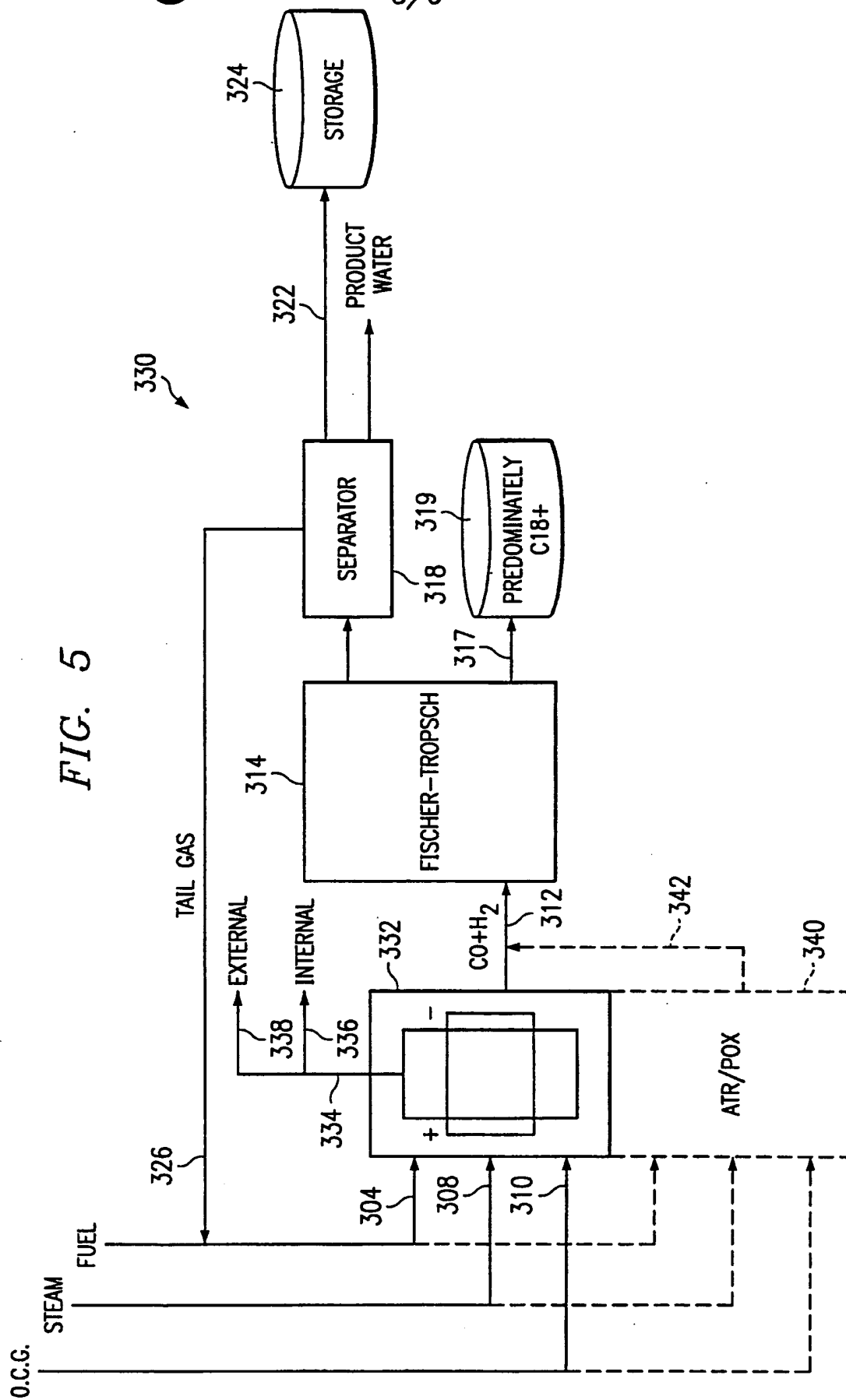


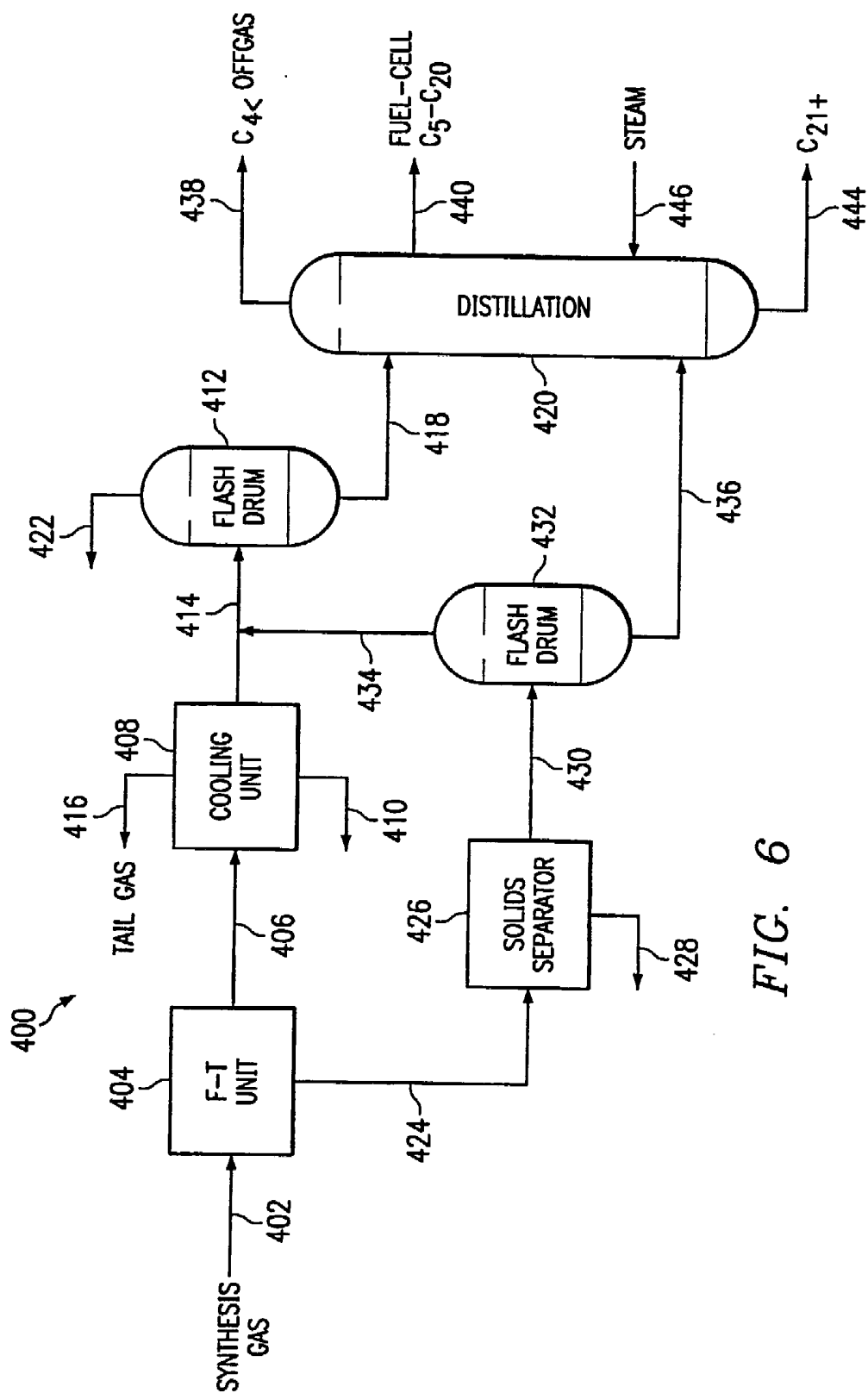
FIG. 2





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INTERNATIONAL SEARCH REPORT

International application No.

500/08299

A. CLASSIFICATION OF SUBJECT MATTER

IPC(7) :C10L 1/00, 1/04, 1/16; C10M 101/02; H01M 8/00, 8/04, 8/18

US CL :585/1, 2, 14; 208/14, 15; 429/13, 17, 19

According to International Patent Classification (IPC) or to both national classification and IPC

B. FIELDS SEARCHED

Minimum documentation searched (classification system followed by classification symbols)

U.S. : 585/1, 2, 14; 208/14, 15; 429/13, 17, 19

Documentation searched other than minimum documentation to the extent that such documents are included in the fields searched

Electronic data base consulted during the international search (name of data base and, where practicable, search terms used)

WEST

search terms: Fischer-Tropsch, fuel cell, paraffin, isoparaffin

C. DOCUMENTS CONSIDERED TO BE RELEVANT

Category*	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
X — Y	US 5,766,274 A (WITTENBRINK ET AL) 16 June 1998 (16/06/98), See column 1, lines 9-21 and 49-66, column 2, lines 23-38 and 64-67 and column 5, lines 15-25.	1-11, 14-16, 18, 19, 22-26, 28, 33 ----- 34-44
X — Y	US 5,689,031 A (BERLOWITZ ET AL) 18 November 1997 (18/11/97), See column 1, lines 9-21 and 45-66, column 2, lines 1-10 and 35-38, column 4, lines 6-20 and column 5, lines 40-45.	1-11, 14-16, 18, 19, 22-26, 28, 33 ----- 34-44
X	US 3,986,349 A (EGAN) 19 October 1976 (19/10/76), See column 4, lines 10-16, column 5, lines 15-40, column 6, lines 49-60 and column 7, lines 55-66.	1, 6, 12, 13, 17, 20, 21



Further documents are listed in the continuation of Box C.



See patent family annex.

* Special categories of cited documents:	"T" later document published after the international filing date or priority date and not in conflict with the application but cited to understand the principle or theory underlying the invention
"A" document defining the general state of the art which is not considered to be of particular relevance	"X" document of particular relevance; the claimed invention cannot be considered novel or cannot be considered to involve an inventive step when the document is taken alone
"E" earlier document published on or after the international filing date	"Y" document of particular relevance; the claimed invention cannot be considered to involve an inventive step when the document is combined with one or more other such documents, such combination being obvious to a person skilled in the art
"L" document which may throw doubts on priority claim(s) or which is cited to establish the publication date of another citation or other special reason (as specified)	"&" document member of the same patent family
"O" document referring to an oral disclosure, use, exhibition or other means	
"P" document published prior to the international filing date but later than the priority date claimed	

Date of the actual completion of the international search

05 SEPTEMBER 2000

Date of mailing of the international search report

19 SEP 2000

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INTERNATIONAL SEARCH REPORT

International Publication No.

PCT/US00/

C (Continuation). DOCUMENTS CONSIDERED TO BE RELEVANT

Category*	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
X	US 4,125,566 A (TRIN DINH ET AL) 14 November 1978 (14/11/78), See column 1, lines 52-68, column 2, lines 5-15 and 48-60.	25-27, 29-32
Y	US 4,522,894 A (HWANG ET AL) 11 June 1985 (11/06/85), See column 3, lines 19-25 and 50-68 and column 4, lines 60-64.	34-44
Y	US 5,660,940 A (LARSSON ET AL) 26 August 1997 (26/09/97), See column 1, lines 9-15 and 49-55.	34-44
A	US 5,401,589 A (PALMER ET AL) 28 March 1995 (28/03/95), See entire document.	34-44
A,E	US H1,849 A (FOURIE ET AL) 02 May 2000 (02/05/00), See entire document.	1-44
A	US 5,362,378 A (BORGHARD ET AL) 08 November 1994 (08/11/94), See entire document.	1-33
A	US 4,500,417 A (CHEN ET AL) 19 February 1985 (19/02/85), See entire document.	1-33
A	US 5,292,983 A (SIE) 08 March 1994 (08/03/94), See entire document.	1-33

INTERNATIONAL SEARCH REPORT

International application No.

/US00/08299

Box I Observations where certain claims were found unsearchable (Continuation of item 1 of first sheet)

This international report has not been established in respect of certain claims under Article 17(2)(a) for the following reasons:

1. ☒ Claims Nos.: 45
because they relate to subject matter not required to be searched by this Authority, namely:

The claim does not define the specific invention to be searched.
2. ☒ Claims Nos.: 45
because they relate to parts of the international application that do not comply with the prescribed requirements to such an extent that no meaningful international search can be carried out, specifically:

The claim does not define specific limitations which can be searched. As a result, it is unclear what specific limitations are encompassed by the claimed invention.
3. ☐ Claims Nos.:
because they are dependent claims and are not drafted in accordance with the second and third sentences of Rule 6.4(a).

Box II Observations where unity of invention is lacking (Continuation of item 2 of first sheet)

This International Searching Authority found multiple inventions in this international application, as follows:

1. ☐ As all required additional search fees were timely paid by the applicant, this international search report covers all searchable claims.
2. ☐ As all searchable claims could be searched without effort justifying an additional fee, this Authority did not invite payment of any additional fee.
3. ☐ As only some of the required additional search fees were timely paid by the applicant, this international search report covers only those claims for which fees were paid, specifically claims Nos.:
4. ☐ No required additional search fees were timely paid by the applicant. Consequently, this international search report is restricted to the invention first mentioned in the claims; it is covered by claims Nos.:

Remark on Protest

- ☐ The additional search fees were accompanied by the applicant's protest.
☐ No protest accompanied the payment of additional search fees.

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